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[Page 1 of 2]

Date 9/5/03

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Dated: September 5, 2003

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R-7695 (1339-5)

**NANOCOMPOSITE FIBERS AND FILMS CONTAINING
POLYOLEFIN AND SURFACE-MODIFIED CARBON NANOFIBERS**

GOVERNMENT RIGHTS

This invention was made with Government support under U.S. Army Research Office Grant DAAD190010419 and NSF Grants DMR9984102 AND DMR0098104. The Government has certain rights in the invention.

BACKGROUND

Nanofiber technology has not yet developed commercially and, therefore, engineers and entrepreneurs have not had a source of nanofibers to incorporate into their designs. Uses for nanofibers will grow with improved prospects for cost-efficient manufacturing, and development of significant markets for nanofibers is almost certain in the next few years. The leaders in the introduction of nanofibers into useful products are already underway in the high performance filter industry. In the biomaterials area, there is a strong industrial interest in the development of structures to support living cells. The protective clothing and textile applications of nanofibers are of interest to the designers of sports wear, and to the military, since the high surface area per unit mass of nanofibers can provide a fairly comfortable garment with a useful level of protection against chemical and biological warfare agents.

Carbon nanofibers are potentially useful in reinforced composites, as supports for catalysts in high temperature reactions, heat management, reinforcement of elastomers, filters for liquids and gases, and as a component of protective clothing. Nanofibers of

carbon or polymer are likely to find applications in reinforced composites, substrates for enzymes and catalysts, applying pesticides to plants, textiles with improved comfort and protection, advanced filters for aerosols or particles with nanometer scale dimensions, aerospace thermal management application, and sensors with fast response times to changes in temperature and chemical environment. Ceramic nanofibers made from polymeric intermediates are likely to be useful as catalyst supports, reinforcing fibers for use at high temperatures, and for the construction of filters for hot, reactive gases and liquids.

Nanofibers having enhanced mechanical and electrical characteristics, including enhanced strength and fire retardant capabilities, are desirable.

SUMMARY

In accordance with the present disclosure, unique synthetic techniques have been developed for the modification of carbon nanofibers where aliphatic linkers of tailored length are covalently bonded to the carbon nanofiber surface. The surface modification process and consequent compounding can be implemented using standard melt-mixing or solution mixing equipment and results in modified carbon nanofibers with enhanced compatibility with polyolefins. The nanocomposite of organo-modified carbon nanofibers and polyolefin matrix can enable the design, development and creation of new fibers and films.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a scanning electron microscope image of the cross-section of a nanocomposite fiber produced in accordance with the present disclosure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with the present disclosure, a unique synthetic scheme has been developed to modify the surface of carbon nanofibers with oligomeric aliphatic linkers of tailored length, which facilitate the dispersion of the modified carbon nanofibers in polyolefins.

In accordance with the present disclosure, carbon nanofibers are functionalized to enhance their compatibility with polyolefins. The modified carbon nanofibers (sometimes referred to herein as MCNF) have enhanced compatibility with polyolefins and the combination of carbon nanofiber and polyolefin can be used to produce fibers and films having enhanced mechanical and electrical properties.

Carbon nanofibers (CNFs) are known to those skilled in the art and are commercially available from numerous sources including, e.g., Pyrograf Products, Inc.

Preferably, to enhance the modification of the carbon nanofibers, surface acidic groups (carboxylic acid and hydroxyl) on the carbon nanofibers are generated by oxidation reaction with a strong acid. Suitable strong acids include potassium perchlorate, sulfuric acid, hydrochloric acid, and combinations thereof. The nanofibers are subjected to this acid treatment at a temperature ranging from about 0 °C to about 100 °C, with a temperature of about 20 °C to about 60 °C being preferred. The oxidation step generates carboxylic acid (-COOH) or sulfonic acid (-OSO₃OH) moieties at the carbon fiber's sidewall.

Once the surface acid groups have been generated, a polymerization initiator is added and attached to the nanofiber. Suitable polymerization initiators are known to

those skilled in the art and include, but are not limited to, 1-(Benzylxyloxy)-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (TEMPO-ester) and 1-Hydroxy-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (TEMPO-alcohol).

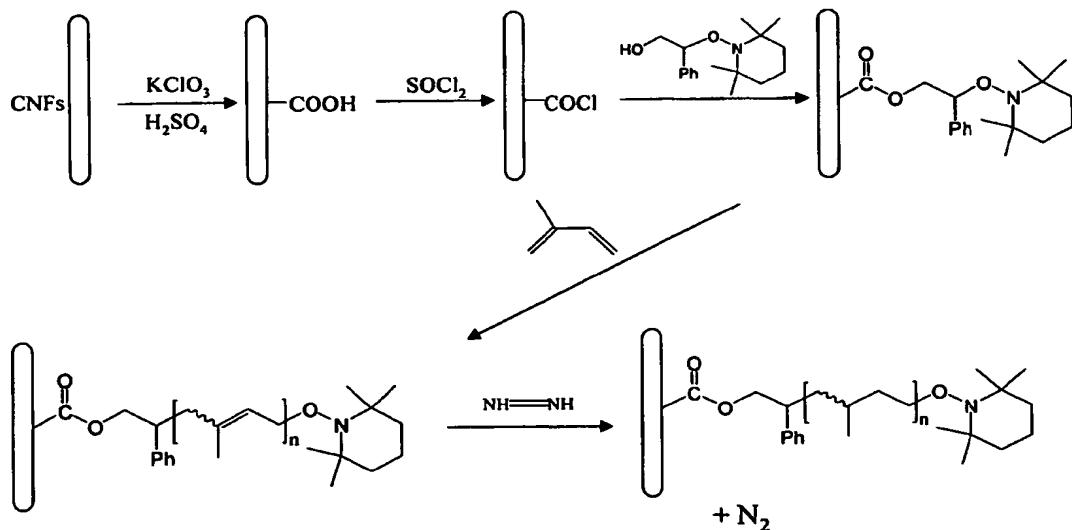
In some embodiments, conventional catalysts, such as triethylamine (TEA), are added at a temperature ranging from about 20 °C to about 90 °C, preferably from about 70 °C to about 80 °C, for a period time ranging from about 1 hour to about 5 days, more preferably from about 1 day to about 3 days.

The reaction mixture is then washed, preferably with water, tetrahydrofuran (THF), or mixtures thereof, and dried *in vacuo* at a suitable temperature, preferably ranging from about 20 °C to about 90 °C, more preferably from about 65 °C to about 75 °C.

The resulting initiator-attached CNFs are then allowed to polymerize. An alkene, preferably a vinyl based alkene such as isoprene, butadiene, or isobutadiene is mixed with the initiator-attached CNFs at a mole ratio of initiator to monomer ranging from about 0.5:600, more preferably from about 1:480. The mixture is preferably heated to a temperature ranging from about 90 °C to about 180 °C, preferably from about 110°C to about 150°C, for a period time ranging from about 5 hours to about 15 hours, more preferably from about 8 to about 12 hours. After the polymerization, the resulting grafted CNFs are washed with methanol and dried *in vacuo* at a suitable temperature, preferably ranging from about 50 °C to about 100 °C, more preferably from about 65 °C to about 75 °C.

The grafted CNFs are then introduced into a suitable solvent such as xylene. Crosslinkers known to those skilled in the art, such as *p*-toluenesulfonyl hydrazide, tri-

n-propyl amine, and combinations thereof can then be added to the solution mixture containing the grafted CNFs. The mixture is preferably heated to reflux at a temperature ranging from about 100 °C to about 180 °C, more preferably from about 120 °C to about 160 °C for a time ranging from about 2 to about 6 hours, more preferably about 3 to about 5 hours. The solution is then preferably filtered, washed with deionized water and methanol, and dried *in vacuo* at a temperature ranging from about 70 °C to about 110 °C, more preferably from about 80 °C to about 100 °C. The modification scheme of the carbon nanofibers to produce the MCNFs is shown below:



The modified carbon nanofibers have enhanced compatibility with polyolefins and can be dispersed at the molecular level to produce composite mixtures. Suitable polyolefins include polyethylene, polypropylene, ethylene-propylene copolymers and ultra-high molecular weight polyethylene. Other polyolefins include High Pressure, Low

Density Polyethylenes (LDPE); Linear Low and Medium Density Polyethylenes (LLDPE); High Density Polyethylenes (HDPE); and Modified Polyethylenes.

The nanocomposites of polyolefin/modified carbon nanofiber can be made by methods known to those skilled in the art. They can be either melt-spun or gel-spun into fibrous form, or melt-cast or gel-cast into film form, with or without uni-axial/bi-axial stretching for alignment of the modified carbon nanofibers. This minimizes stress to the modified carbon nanofibers and results in improved mechanical and electrical properties as well as improved fire retardant properties.

In one embodiment, modified carbon nanofiber nanocomposite may be produced by a two-step procedure. In such a case the polyolefin can be blended with the modified carbon nanofibers in a solution blending process whereby the modified carbon nanofibers are blended with the polyolefin in a suitable solvent, e.g. xylene and then precipitated in cold methanol. For the solution blending step, a conventional blending device such as a Henschel® mixer, or a soaking device such as a simple drum tumbler can be used.

The dried precipitants can then be melt-blended to form the nanocomposites of the present disclosure. For the melt blending step, the mixture is heated to melting while agitating the mixture, and cooling the nanocomposite. Examples of equipment used in melt blending methods include co-rotating and counter-rotating extruders, disc-pack processors and other commonly used extrusion equipment. Other equipment that may be used include roll mills, biaxial screw kneading extruders, or Banbury® or Brabender® mixers. In one embodiment, the melt blending is accomplished by introducing the dry precipitants into a DACA twin-screw micro-compounder at 190 °C for 3 minutes under

the presence of antioxidant Irgonox 3114. Other antioxidants known to those skilled in the art may also be used.

In another embodiment, solution blending of the polyolefin and modified carbon nanocomposite can occur in a one-step process. In such a case, the modified carbon nanofiber and polyolefin can be introduced in paraffin oil or similar material at 130 °C and the resulting nanocomposite can later be precipitated in cold methanol.

The resulting nanocomposite may then be used to form fibers or films using commercially available equipment and techniques. In one embodiment, a preferred method for spinning nanocomposite fibers of the present disclosure is set forth in Ran et al., "In-Situ Synchrotron SAXS/WAXD of Melt Spinning of Modified Carbon Nanofiber and Polypropylene Nanocomposite", from ACS PMSE, 89, 735-736 (2003), the contents of which are incorporated by reference herein, and a copy of which is attached hereto.

While the above disclosure has focused on the modification of carbon nanofibers and their combination with polyolefin matrices to produce nanocomposites of the present disclosure, other materials, such as carbon nanotubes, can also be modified in accordance with the methods of the present disclosure and combined with polyolefin matrices to produce comparable nanocomposites.

The following non-limiting examples are provided to illustrate the methods described herein.

EXAMPLES

Polyolefin Matrices and Carbon Nanofibers (CNFs) were produced utilizing the following materials. Isotactic polypropylene (iPP) pellets were an experimental resin provided by Exxon-Mobil Company, having a weight average molecular weight about

350,000 g/mol. The ultra high molecular weight polyethylene (UHMWPE) powders were obtained from Basell, USA, having a molecular weight about 5,000,000 g/mol. The carbon nanofiber (CNF, PR-24-HHT) was obtained from Pyrograf Products, Inc., which had undergone a severe thermal treatment to remove any non-carbon material. The typical morphology of the as-received CNFs had an average diameter of 70 nm and a length of 50-100 μ m. The CNFs were clean, so no additional purification procedures were taken in this study.

All reagents were purchased from Aldrich, Acros, and the solvents purchased were from Fisher Scientific. Styrene and Triethylamine (TEA) were distilled from CaH₂. Tetrahydrofuran (THF) was dried by sodium under nitrogen. Other reagents were used without purification. Silica gel for flash chromatography was Merck grade 60 (70-230). The polymerization initiators, 1-(Benzylxy)-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (TEMPO-ester) and 1-Hydroxy-2-phenyl-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (TEMPO-alcohol), were synthesized according to procedures known to those skilled in the art.

EXAMPLE 1

Acid group generation on carbon nanofibers. The surface acidic groups (carboxylic acid and hydroxyl) on the carbon nanofibers were generated by oxidation reaction with potassium perchlorate/sulfuric acid solution (e.g. 2 g of carbon nanofibers in KClO₃ solution (2 g of KClO₃/100 ml of concentrated H₂SO₄)) at room temperature. The carbon nanofiber suspension was filtered by 0.2- μ m membrane and washed with deionized water and methanol. The filtered nanofibers were dried *in vacuo* at 70 °C.

EXAMPLE 2

Attachment of radical initiator to the carbon nanofiber surfaces. The oxidized CNFs from Example 1 were refluxed in thionyl chloride for 24 hours at 65 °C, then the thionyl chloride was removed by distillation. The dried acyl chloride CNFs were reacted with TEMPO-alcohol in the dry THF using TEA as a catalyst at 75 °C for 2 days. The reaction mixture was washed with water and THF and dried *in vacuo* at 70 °C.

EXAMPLE 3

Surface free radical polymerization. The initiator-attached CNFs produced in Example 2 were mixed with isoprene (mole ratio of initiator to monomer is about 1:480). The mixture was heated at 130 °C for 10 hours. After the polymerization, the grafted CNFs were washed with methanol and dried *in vacuo* at 70 °C.

EXAMPLE 4

Reduction of the grafted polymer. The grafted CNFs or Example 3 were dispersed in xylene. *p*-toluenesulfonyl hydrazide and tri-*n*-propyl amine were added to the solution mixture. The mixture was heated to reflux at 140 °C for 4 h. The solution was filtered, washed with deionized water and methanol, and dried *in vacuo* at 90 °C.

EXAMPLE 5

Nanocomposite preparation. In order to obtain homogenous iPP/modified carbon nanofiber nanocomposite, two-step procedures were used to blend iPP with the modified

carbon nanofibers produced in Example 4. The first step was solution blending, in which 5%, 20% and 50% (weight) modified carbon nanofibers were blended with iPP in xylene at 130 °C and then precipitated in the cold methanol. The dried precipitants were then melt-blended to form composite by a DACA twin-screw micro-compounder at 190 °C for 3 min under the presence of antioxidant Irgonox 3114.

A similar one-step process was also used to prepare UHMWPE/modified carbon nanocomposite. Solution blending of 5%, 20% and 50% (weight) modified carbon and UHMWPE in paraffin oil at 130 °C was carried out and nanocomposite samples were precipitated in the cold methanol.

EXAMPLE 6

Nanocomposite fiber spinning. The melt spinning process of iPP/modified carbon nanofiber (MCNF) nanocomposite fiber was carried out using a custom-built spinning apparatus. In this apparatus, a capillary rheometer-like barrel was located on the top platform, which held the polymer composite melt with an upper temperature capability of about 350 °C. A motor driven plunger was used to extrude the polymer composite melt. A take-up wheel with an adjustable speed control provided the means to change the spin draw ratio (SDR), defined as the ratio of the fiber take-up speed to the extrudate speed at the spinneret exit. The melt extrusion temperature of iPP/modified carbon nanofiber nanocomposite was set at 195 °C. Scanning electron microscope images of the nanocomposite fiber were obtained. The SEM image of the cross-section of the nanocomposite fiber, which is set forth in Figure 1, clearly showed that the MCNFs were

dispersed mostly as single fibers, not as bundles, indicating that the surface modification was successful.

The gel spinning process of UHMWPE/modified carbon nanofiber nanocomposite fiber was carried out using the same custom-built spinning apparatus. Gel solutions of 5 wt% of UHMWPE/modified carbon nanofiber nanocomposite of different composition ratios in paraffin oil were prepared for this study. The gel spinning temperature was set at 130 °C.

While the above description contains many specific details of methods in accordance with this disclosure, these specific details should not be construed as limitations on the scope of the disclosure, but merely as exemplifications of preferred embodiments thereof. Those skilled in the art will envision many other possible variations that all within the scope and spirit of the disclosure.

In-Situ Synchrotron SAXS/WAXD of Melt Spinning of Modified Carbon Nanofiber and Polypropylene Nanocomposite

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INTRODUCTION

Single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have been considered as good nanofiller materials to create a new class of high performance polymer fibers due to their high strength at lightweight, small diameter (~ 1 nm for SWNTs and 2 ~ 50 nm for MWNTs), and asymmetric aspect ratios^[1]. However, with the current production technology, these materials are too expensive for practical use. One alternative nanofillers material is the much less expensive vapor grown carbon nanofibers (CNFs), which have an average diameter of (50–200 nm) in between the diameter of conventional carbon fibers (7 ~ 10 μm) and those of SWNTs and MWNTs.

Several polymer nanocomposites based on CNFs have been demonstrated, including isotactic polypropylene (iPP)^[2,3], polycarbonate^[4] and nylon^[5]. In these studies, while the potential benefits of mechanical reinforcement were seen, the major challenge is also clear in the preparation of the composites. With the carbon nanofibers being entangled in the solid state and forming a dense, robust network structure, it is essential to devise effective pathways to achieve good carbon nanofiber dispersion in the polymer matrix at sufficiently high carbon nanofiber concentrations.

In this work, the surface of CNFs was modified to increase the interfacial compatibility between carbon nanofibers and the iPP matrix. The composite of iPP and modified carbon nanofiber (MCNF) was prepared by physical blending. The structural development of the composite fiber during spinning was investigated by synchrotron small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) techniques, which have been demonstrated in our laboratory^[6,7].

EXPERIMENTAL

The iPP pellets were an experimental resin provided by Exxon-Mobil Company. The carbon nanofiber (PR-24-HHT) was obtained from Pyrograf Products, Inc., which had an average diameter of 70 nm and a length of 50–100 μm . 5% (weight) modified carbon nanofibers were blended with iPP by a twin-screw micro-compounder at 190 °C.

The *in-situ* fiber spinning study was carried out using a custom-spinning apparatus constructed in our laboratory. A photograph of this modified apparatus used for the *in-situ* synchrotron WAXD experiment is shown in Figure 1. In this apparatus, a capillary rheometer-like barrel was located on the top platform, which held the polymer composite melt with an upper temperature capability of 350 °C. A motor-driven plunger was used to extrude the polymer composite melt. The top platform could be moved vertically, allowing the detection spot along the spin line to be changed. The apparatus was mounted on a pair of precision optical rails perpendicular to the X-ray beam, which permitted the alignment of the monofilament fiber with the X-ray beam. A take-up wheel with an adjustable speed control provided the means

to change the spin draw ratio (SDR), defined as the ratio of the fiber take-up speed to the extrude speed at the spinneret exit.

The spinning experiment was carried out in the ChemMat CARS at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The wavelength used was 0.75 Å for WAXD and 1.50 Å for SAXS. The 3rd-generation synchrotron X-ray beam at the APS was so strong that 5 sec of exposure of the monofilament fiber with a diameter of ~6–10 μm was sufficient to yield good structural information. The real-time measurements during fiber spinning were carried out using a Bruker CCD X-ray detector. The distance between the detector and the sample for WAXD was 59.59 mm, which was calibrated using an Al₂O₃ standard. For SAXS, the distance between the detector and the sample was 1903.7 mm. The melting spinning study of iPP/MCNF was carried out at 195 °C. The extrusion speed at the spinneret was fixed at 5.2 mm/sec.

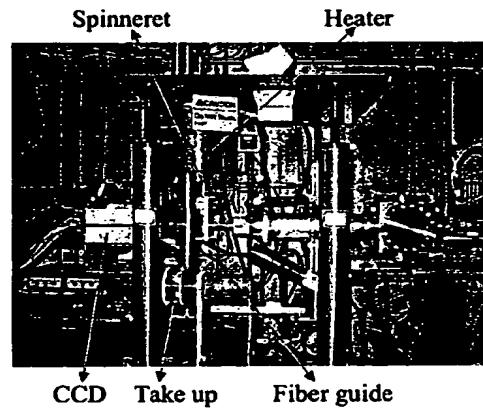


Figure 1. WAXD setup of spinning apparatus at the ChemMat CARS of APS/ANL.

RESULTS AND DISCUSSION

Figure 2 shows the two-dimensional (2D) WAXD patterns of the iPP/MCNF composite fiber at different spin draw ratios after correction of the air scattering. These patterns showed well-resolved diffraction peaks, typical of the α -form iPP crystals. With increasing spin draw ratio, the azimuthal spreads of the reflection peaks became much narrower, indicating that the crystal orientation was increased. Since the diffraction peaks of the pure carbon nanofiber are very close to some of the iPP reflections, it is not easy to distinguish the MCNF from iPP in the composite WAXD patterns at low spin draw ratios. Fortunately, at high spin draw ratios (SDR=31 and 60), the 002 reflection of the CNF was clearly observed because of the difference in the orientation between iPP and MCNF. It should be noted that we used the designation "002" only because of its familiarity from graphite. The implied ABA stacking sequence of the carbon layers is usually not found in MWNTs or CNFs. It was seen that the MCNF was only partially oriented in the composite at high spin draw ratios.

One of the advantages in conducting the experiments in the ChemMat Cars/APS was that the wavelength could be easily adjusted. The relatively short wavelength (0.75 Å) chosen in this work allowed the second scattering ring of the CNF (reflection (10)) to be seen, although it was very weak. It was interesting to note that the orientation of the iPP reflection (040) was much higher than that of the reflection (110) at low spin draw ratios. At high spin draw ratios, the orientation of (110) and (040) were almost the same, which indicated that the orientation of (110) and (040) developed differently during the fiber spinning. The calculation of the Hermans' orientation factor P_2 of reflections (110) and (040) confirmed this observation.

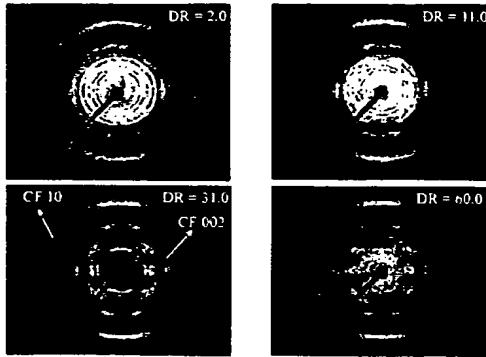


Figure 2. 2D WAXD patterns of the composite fiber at different spin draw ratios after correction of air scattering.

The chain axis orientation of the fiber was calculated mathematically by using the following equations.

$$\langle \cos^2 \phi_{c,z} \rangle = 1 - 1.099 \langle \cos^2 \phi_{10,z} \rangle - 0.901 \langle \cos^2 \phi_{00,z} \rangle$$

$$\langle P_2(\cos \phi_{c,z}) \rangle = \frac{3 \langle \cos^2 \phi_{c,z} \rangle - 1}{2}$$

with Z being the direction of the fiber axis.

Figure 3 shows the calculated Hermans' orientation factor P_2 along the chain axis for both composite fiber and pure iPP fiber. It was found that at low spin draw ratios, the 5%MCNF reinforced iPP composite fiber had much higher orientation than the control iPP fiber, indicating that the modified carbon nanofibers facilitated the orientation of iPP chains at low spin draw ratios. When the spin draw ratios were very high, the orientations of the composite fiber and the pure iPP fiber were almost the same and all reached very high orientations ($P_2=0.9$).

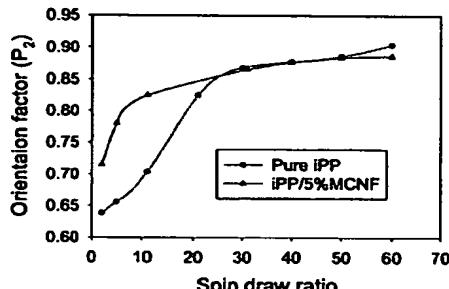


Figure 3. Hermans orientation factor of chain axis for both composite fiber and pure iPP fiber at different spin draw ratios.

Figure 4 shows the 2D SAXS patterns of the composite fiber at different spin draw ratios. The patterns showed a meridionally aligned two point pattern, indicating the presence of lamellar structure of iPP with the lamellar normal preferentially aligned about the fiber axis. The 2nd order of the scattering peak was very clear in the higher q range. The long period was obtained from the Lorentz-corrected peak maxima. The values showed that the composite fiber formed a larger long period at low spin draw ratios. At high draw ratios, the long period of the composite fiber was similar to that of the pure iPP. On the equator, the composite fiber showed a strong diamond shaped SAXS pattern, while the pure iPP fiber showed a typical equatorial streak due to the fibrillar superstructure. The pure carbon nanofiber showed a

butterfly shaped pattern due to the organization of needle-like voids. The difference in the SAXS patterns indicated that the surface modification of the CNF strongly changed the interfaces between the MCNF and iPP matrix.

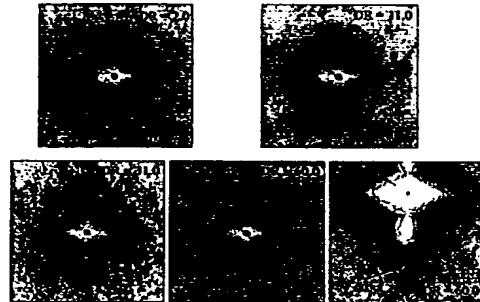


Figure 4. 2D SAXS patterns of the composite fiber at different spin draw ratios.

A bundle of the spun fibers with SDR of 50.0 was used to measure the tensile mechanical properties. The stretching speed was 20 mm/min. Table 1 shows the tensile strength, Young's modulus and elongation to break of the composite fiber and the pure iPP. It was found that the composite fiber with 5% MCNF had much higher tensile strength, modulus and longer elongation to break. It was evident that the surface modification of carbon nanofibers successfully increased the interactions between carbon nanofiber and the iPP matrix, thereby enhancing the homogenous dispersion of the carbon nanofibers in the matrix and the mechanical performance.

	Pure iPP			iPP/5%MCNF		
	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
Average	175 ± 20	2.87 ± 0.5	321 ± 40	319 ± 36	4.53 ± 0.7	533 ± 70

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CLAIMS:

1. A method for modifying carbon nanofibers to provide enhanced compatibility with polyolefins in accordance with the above disclosure.
2. A nanocomposite of organo-modified carbon nanofibers and a polyolefin matrix in accordance with the above disclosure.
3. The nanocomposite of claim 2 wherein the nanocomposite is a fiber.
4. The nanocomposite of claim 2 wherein the nanocomposite is a film.

ABSTRACT

Methods for modifying carbon nanofibers with organic compounds are disclosed.

The modified carbon nanofibers have enhanced compatibility with polyolefins.

Nanocomposites of the organo-modified carbon nanofibers and polyolefins can be used to produce both fibers and films having enhanced mechanical and electrical properties.

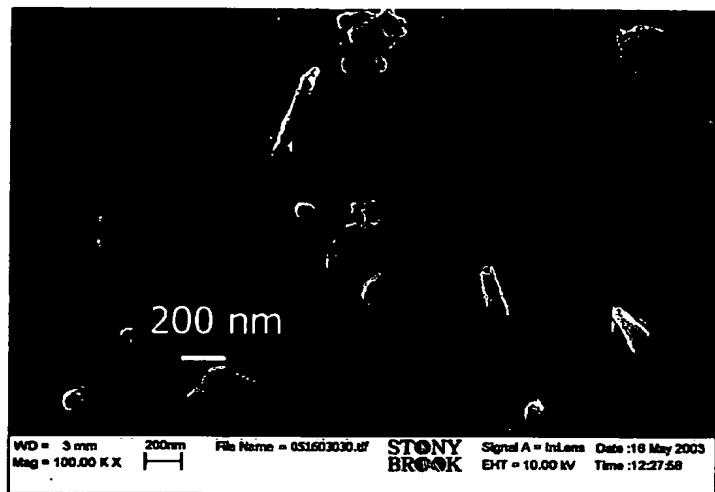


FIG. 1